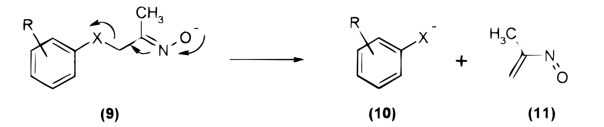

Figure 3. Mechanism of oxime fragmentation.

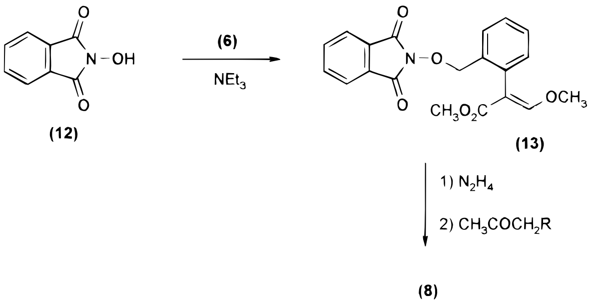

Figure 4. Preparation of extended strobilurins of type **8**.

5) with *N*-chlorosuccinimide followed by sodium methane thiolate to give the oxime **15**. Reaction of **15** with **6** in the presence of sodium hydride, followed by oxidation of the sulfur and displacement of methylsulfonate with the alkoxy/thioalkoxy anion afforded the desired products, **16**.[6]

A further class of active strobilurins prepared were the 'oxyamidines' (**19**, Fig 6). These were synthesized by the reaction of a variety of anilines (**17**, Fig 6) or heterocyclic equivalents with trimethylorthoformate and zinc chloride to give the imidates **18**. Reaction of the oxyphthalimide **13** with hydrazine followed by **18** produced the desired products, **19**.[7]

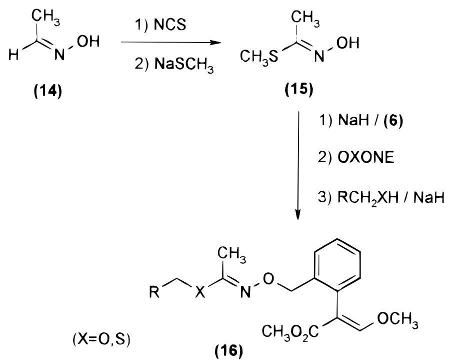

Figure 5. Preparation of extended strobilurins (**16**).

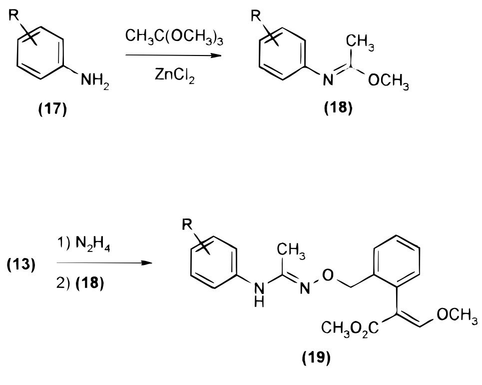

Figure 6. Preparation of oxyamidines **19**.

Good levels of activity amongst all three series of strobilurins was found against a broad spectrum of fungal pathogens in glasshouse tests, examples being *Erysiphe graminis* DC, *Plasmopara viticola* Berl & de Toni and *Septoria nodorum* Berk. The 'oxyamidine' series (**19**) also showed excellent activity against *Puccinia recondita* Rob.ex Desm. and *Venturia inequalis* (Cooke) Wint.

REFERENCES

1 Mansfield RW and Wiggins TE, Photoaffinity labelling of β-methoxyacrylate binding site in bovine heart mitochondrial cytochrome bc_1 complex. *Biochim Biophys Acta* **1015**:109 (1990).
2 Clough JM and Godfrey CRA, *Chemistry in Britain*, pp 466–469 (1995).
3 deFraine PJ and Clough JM, A new series of broad-spectrum β-methoxyacrylate fungicides with an oxime ether side-chain. *Pestic Sci* **44**:77–79 (1995).
4 EP 043488 (BASF).
5 Aspinall IH and Worthington PA, WO 94/08948 (Zeneca).
6 Aspinall IH and Worthington PA, WO 94/14761 (Zeneca).
7 Aspinall IH and Worthington PA, WO 94/14322 (Zeneca).

The effects of six adjuvants on the rainfastness of chlorpyrifos formulated as an emulsifiable concentrate

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Abstract: The chemically different adjuvants 'Agral', 'Bond', 'Codacide Oil', Li 700, 'Silwet L'-77, and 'Headland Guard' were assayed to determine their effects on the rainfastness of an emulsifiable concentrate formulation of the organophosphorus pesticide chlorpyrifos. Cabbage leaves were each treated with 200 × 0.25-μl droplets of diluted formulation using a hand-held microapplicator. Droplet deposits were left to air-dry for 1 h prior to exposure to simulated rainfall. Rain fastness was assessed using GC residue analyses of treated leaves after exposure to 10, 20 or 30 min simulated rainfall. The results indicated that the latex-based adjuvants 'Bond' and 'Headland Guard' induced a statistically significant increase in rainfastness, results for the other adjuvants assayed being either not significant or inconclusive. The results are discussed within the context of using adjuvants to enhance insecticide efficacy.

Keywords: rainfastness; chlorpyrifos; adjuvants; organophosphate

1 INTRODUCTION

To maximise their biological efficacy many pesticides have to be able to withstand, following applica-

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tion, weathering due to wind, rain, dew formation, and exposure to UV radiation.[1,2] Of all these factors, rainfall has been reported as having the greatest effect upon the residual activity of a pesticide[3] and numerous authors have reported on the effects of rainfall on persistence of deposits.[1–6]

Rainfall may affect the activity of a deposit by dilution, redistribution, physical removal, and by the extraction of pesticide from the plant tissue. Overall rainfastness will depend upon which combination of these factors is at work, as well as the time between application and the onset of rainfall, the type of rainfall, the formulation, and the properties of the target surface.

Clearly, the simplest way to avoid rain-induced wash-off is to spray when rainfall is unlikely. This, however, is not always possible. For example, insecticides are applied to tobacco plants in Zimbabwe during the rainy season and under such circumstances any increase in the rainfastness of the formulation would be of considerable help.[7] Our aim in the work described in this summary was to investigate formulation changes in relation to rainfastness. To change the formulation we added one of six commercially available adjuvants to an organophosphorus pesticide application.

Published material concerning the use of adjuvants to enhance rainfastness has mostly described research where bioassays have been used to evaluate potential biological activity. However, we aimed to measure exactly the proportion of active ingredient that was removed following exposure to simulated rainfall by GC analyses of leaves that had been treated with a known amount of pesticide.

2 METHODS

The commercial chlorpyrifos 480 g litre^{-1} EC 'spannit' (PBI) was diluted with distilled water and used at the manufacturer's recommended rate of application for Lepidoptera control on brassicas. The adjuvants used are described in Table 1.

Individual cabbage leaves were treated with 200 × 0.25-µl droplets of diluted formulation, either with or without each adjuvant, using a hand-held microapplicator. Leaves were left to air-dry for 1 h prior to exposure to simulated rainfall. Four replicate leaves were held at an angle of 45° and then exposed to simulated rainfall for 10, 20, or 30 min using an Azo compressed air hydraulic sprayer fitted with Teejet 100° flat fan nozzles. Tap water was sprayed at a pressure of 2 bar from the boom which was suspended at a height of 1.5 m directly above the cabbage leaves. Intensity of rainfall, expressed as ml cm^{-2} per minute, was recorded during each spray appliction.

Following spraying, treated leaves were homogenised individually in residue analysis grade acetone using a pestle and mortar. Acid-washed sand provided an abrasive substance to aid this process. The homogenate was then transferred to a 50-ml centrifuge tube and an internal standard (chlorpyrifos-methyl) added, after which the mixture was spun at 2000 rev min^{-1} for 5 min and the supernatant poured off for GC residue analysis. Aliquots (0.5 µl) of each sample were injected into a Perkin Elmer PE8500 GC fitted with an electron-capture detector and the amount of chlorpyrifos present within each sample was calculated by comparing its peak with that of the internal standard. This was achieved by first calculating the detector-response factor for a solution containing known amounts of both compounds, this being a constant calculated from the ratio of the two peak areas. The factor was then used to calculate the unknown amount of chlorpyrifos from the known amount of chlorpyrifos-methyl in the internal standard. The resulting data were expressed as the percentage of the deposit that was detected for leaves exposed to no rainfall. One-way analysis of variance was used to analyse each set of the resulting data (with or without each adjuvant).

3 RESULTS AND DISCUSSION

Rainfastness of deposits was significantly enhanced for all treatment times (10, 20 or 30 min) when the latex-based adjuvants Bond and Headland Guard were added to the insecticide ($P < 0.001$). Of these two adjuvants, the better improvements in rainfastness were realised with 'Bond', and these are shown in Fig 1. The figure shows that, for all treatment times, rainfastness of the deposits more than doubled. The figure also shows that there was a negative relationship between the improvement in rainfastness and the duration of rainfall. The duration of rainfall had no effect upon the rainfastness of

Table 1. Adjuvants assayed

Adjuvant	*Chemical composition*	*Application rate (g litre^{-1})*
Agral	Phenol ethylene oxide condensate (480 g litre^{-1})	0.3
Bond	Synthetic latex (450 g litre^{-1})	1.4
Codacide Oil	Vegetable oils and emulsifiers	10
Headland Guard	Organic copolymer and surfactants (55 g litre^{-1})	1.0
Li700	Tallow amine surfactants	5.0
Silwet Lp77	Organosilicone surfactants	0.5

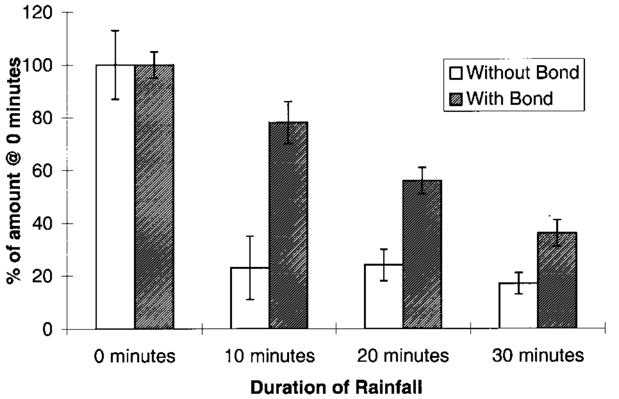

Figure 1. The effect of the adjuvant Bond on the mean amount of chlorpyrifos remaining on cabbage leaves after exposure to 10, 20 or 30 min rainfall. All data are shown as the amount remaining calculated as a percentage of the amount recorded on leaves that were not exposed to rainfall. Bar = SD.

the insecticide alone. Approximately 80% of the insecticide was washed off irrespective of the duration of rainfall. The increases in rainfastness with the other latex-based adjuvant ('Headland Guard') were also statistically significant for all treatment times. However, the improvement in deposit rainfastness with this adjuvant was by a constant factor of *c* 1.75. None of the other adjuvants assayed produced significant improvements in rainfastness for the rainfall treatment times used.

These results, which indicate that latex-based adjuvants can enhance rainfastness, are in broad agreement with other, similar studies that have been reported in the literature.[1,8–10] The main advantage with our approach, however, was that we were able to control exactly how much pesticide was applied to leaves and also to determine exactly how much had been removed. This meant that we were able to quantify the magnitude of the improvements in rainfastness that were realisable with the adjuvants tested. Therefore, our conclusion from these results is that latex-based adjuvants may be able to enhance dramatically the resistance of pesticides to wash-off. In the present work only two latex-based adjuvants were assayed and the work was carried out under laboratory conditions. For the future we intend to repeat these studies with other leaf surfaces and formulations and to undertake larger-scale field trials to assess whether improvements in rainfastness can translate into economic savings for growers via reductions in the number of pesticide applications that need to made to crops.

REFERENCES

1 Taylor N and Matthews GA, Effect of different adjuvants on the rainfastness of bendiocarb applied to brussel sprout plants. *Crop Prot* **5**:250–253 (1986).
2 Omar D and Matthews GA, Influence of formulation and spray droplet size upon the persistence of permethrin deposits on brussel sprout leaves. *Crop Prot* **10**:41–44 (1991).
3 Willis GH and McDowell LL, Pesticide persistence on foliage. *Rev Environ Contam Toxicol* **100**:23–73 (1987).
4 Pick FE, Van Dyk LP and deBeer, PR, The effect of simulated rain on deposits of some cotton pesticides. *Pestic Sci* **15**:616–623 (1984).
5 Nord JC and Pepper WD, Rainfastness of insecticide deposits on loblolly pine foliage and the efficacy of adjuvants in preventing wash-off. *J Entomol Sci* **26**:287–298 (1991).
6 Willis GH, McDowell LL, Southwick LM and Smith S, Wash-off of ultra low volume oil applied insecticides from cotton plants as a function of time between application and rainfall. *J Environ Qual* **21**:373–377 (1992).
7 Mashaya N, Effect of simulated rain on efficacy of insecticide deposits on tobacco. *Crop Prot* **12**:55–58 (1993).
8 Reeves R, The use of a sticker type of adjuvant with insecticides. *Pestic Sci* **37**:206–209 (1993).
9 Collier RA, Use of sticker/surfactant products in a high risk potato blight spray programme. *Pestic Sci* **37**:223–225 (1993).
10 Thacker JRM, Young RDF, Macaskill S, Dixon A, Hall FR and Downer RA, Using spray adjuvants to enhance arthropod pest control. *Rec Res Develop Entomol* **1**:187–202 (1997).

Allium spp thiosulfinates as substitute fumigants for methyl bromide

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Abstract: Methyl bromide, the most widely used fumigant, is considered to be one of the major factors causing depletion of the ozone layer, and this is likely to lead to it being banned in the near future. *Allium* sulfur volatiles (thiosulfinates, R-S-SO-R′; R, R′ = Me, Pr, y Allul), known to be nematicides, have been evaluated as insecticides against insect pests in stored products, in comparison with their degradation compounds (disulfides) which have already been tested. Methyl and allyl thiosulfinates, with 24-h LD_{50} values of 0.02–0.25 mg litre^{-1}, were more active than disulfides against six test insects and were superior to methyl bromide; it is suggested that they could be used as alternatives to methyl bromide in stored product control.

Keywords: *Allium* spp, disulfides; fumigants; insects; methyl bromide; thiosulfinates

1 INTRODUCTION

Insect infestation, mainly by Coleoptera or Lepidoptera, causes major damage and loss during food storage, particularly in tropical areas. The control of such insect populations in stored products poses numerous problems. Mechanical or physical means are not in themselves sufficient. Only fumigants (acting in the gaseous state) are likely to diffuse through, and into, large masses of seeds. These fumigants are very effective on eggs and adults as well as on hidden stages, and leave very little or no residue.

However, chemical fumigants have similar drawbacks to synthetic pesticides used on cultivated crops

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